Torrefaction of Agriculture and Forestry Biomass Using TGA-FTIR-MS

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Abstract

The torrefaction of agriculture (switchgrass and timothy) and forestry (spruce and pine) biomass was studied using simultaneously thermogravimetric analyzer (TGA) coupled with Fourier transform infrared (FTIR), and mass spectrometer (MS). The chemical functional groups present in the gases were identified by FTIR and the quantification of gaseous products was determined using MS at different torrefaction temperatures ranging from 200 to 290 °C. TG-FTIR and TG-MS techniques are paired to refine the identification of gases. TGA results showed that the behavior of the agricultural and forestry biomass was not the same due to their composition variation. The decomposition of switchgrass took place at a lower temperature than other biomass. Both switchgrass and timothy have two peaks of degradation rate compared to only one peak present for forestry biomass. The FTIR analysis indicated that most of the chemical compositions present in the biomass are decomposed at torrefaction temperature of 290 °C. The mass spectrometric analysis at torrefaction temperature 200 and 230 °C quantified the degradation of combustible gases: CH_4, C_2H_4, CO, and O_2 around 20–30 %, whilst at torrefaction temperature 260 and 290 °C the degradation of combustible gases was more than 30 %. Moreover, all gaseous products evolved from the torrefaction of agricultural and forestry biomasses were almost similar in characteristics, but varied in proportions.

Keywords

Agricultural biomass • Forestry biomass • Torrefaction • TG-FTIR

Introduction

Canada is one of the countries in the world which generates abundant amount of biomass from agriculture and forestry sector. Canada has about 42 % of forest land and 6.8 % of agricultural land from which about 42 % of residue is produced entirely from forestry and agricultural [26]. Hence, there exists large potential to convert this biomass into valuable products for various applications. Thermochemical treatment is an effective method to handle the issue of this huge biomass resource. This process has great advantages since it is flexible in feedstock, produces different fuels, and is environmental friendly.

Torrefaction is also emerging as one of thermochemical method to produce energy fuel by improving the biomass properties [1]. The biomass is heated between temperatures 200–300 °C in an inert condition. Torrefaction has been reported [1] to improve the hygroscopic behavior, decay resistivity, grindability, and higher heating value. Moreover, it can help to reduce the greenhouse gas emissions. Assuming a net calorific value of 6.2 MW h/ton, torrefied pellets (4,533,724 ton) is estimated to save CO_2 emissions of 21,081,816 ton, if the former is replaced by traditional pellets (5,736,549 ton) [12]. Despite this saving in emissions, the behavior of biomass torrefaction still needs serious research attention.

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With regard to this, TGA–FTIR technique is the most widely used method to observe the thermal decomposition of materials under various environments. Understanding about the kinetics and an in-depth analysis of mass loss with the type of release of gas products [18] are essential for the fundamental knowledge, design, operation, and control [13] of torrefaction equipment and process. Therefore, the influence of parameters on chemical composition of the torrefied product has been extensively studied. In torrefaction, the lignin network is modified [2, 15, 23], and hemicelluloses are strongly degraded [17] leading to formation of carbonaceous material within the wood [16]. The anhydrous mass loss during torrefaction could be a reliable and accurate indicator to predict dimension stability and decay resistivity of pellet fuel [9, 25].

Some studies were found related to torrefaction of biomass using TG analysis to determine the torrefaction kinetic of cellulose, hemicellulose, lignin, and xylan [6]. The same author has also conducted torrefaction of various biomasses (bamboo, willow, coconut shell, and wood) using TG analysis [7]. Another study also reported which was focused on torrefaction of deciduous wood (beech and willow), coniferous wood (larch), and straw using TG analyzer [19]. Very recently, a study on torrefaction of wheat straw but using TGA/DSC configuration mode was performed [21]. From this and other literature survey, none has attempted to torrefy biomass using TGA coupled with FTIR. Since TGA coupled with FTIR can be advantageous for continuous online gas analysis, the torrefaction thermal decomposition can be studied in depth. It was also difficult to find torrefaction of agriculture (switchgrass and timothy) and forestry (spruce and pine) biomass using TG-FTIR-MS technology. Keeping this in view, the study contributes new knowledge about the characteristics of the gas evolved during torrefaction of various types of biomass. The main objective was to determine the torrefaction behavior as well as simultaneously investigate the chemical functional groups and quantification of the gas product. TG-FTIR-MS analyses of gas were carried out at different temperature of the torrefied biomass. Comparison of torrefaction of agriculture and forestry biomass is presented in this study.

Materials and Method

Four types of biomass were selected for torrefaction. Two were agriculture (switchgrass and timothy) and other two were forestry (spruce and pine). The agricultural biomass samples were provided by NB Department of Agriculture. The forestry biomass chips of size ranging from 10 to 50 mm were acquired from local sawmill. Prior to the analysis, biomasses were first dried in the oven at 105 °C for 24 h, and then grounded to about 500 μm particle size.

TG-FTIR Experiment

A Nicolet 6700 FTIR Thermo Scientific connected to TGA Q500 TA Instrument was used to perform torrefaction experiments. Approximately 10 mg of sample was loaded in a TGA crucible. The temperature was initially raised to 105 °C at heating rate of 20 °C/min and held for 5 min in order to remove moisture. At second stage the samples were torrefied using same heating rate to a desired temperature. The inert atmosphere was maintained using nitrogen gas at flow rate of 100 ml/min. Vapors released from biomass torrefaction were subjected to the FTIR spectrometer through a transfer tube, which is heated to about 200 °C to prevent the condensation of vapors on the tube wall. The IR spectra were recorded with a temporal resolution about 2 s. The resolution of the collected spectra was set to be 1 cm^{-1} and the spectral range was set from 4,000 to 400 cm^{-1}. At the carrier gas flow rate of 100 ml/min, it took about 50 s for the vapors to reach the FTIR cell from the thermogravimetric analyzer. Therefore, there was time delay of about 50 s.

TG-MS Experiment

The volatile products generated from TGA that was first scanned by FTIR spectrometer to detect the functional group, and then were furthered transferred to the ionization source of the mass spectrometer, SRS RGA 200, in order to determine specific chemical compound. The transfer line was heated and maintained at a temperature of 200 ºC to prevent the condensation of the volatile gases released during the torrefaction process. The mass spectrometer is operated at electron energy of 70 eV. The gases were analyzed by using the RGA software. A scan of the m/z was carried out from 1 to 100 amu to determine which m/z has to be followed during the TG experiments. The intensities of ten selected ions (m/z = 15, 16, 27, 28, 29, 32, 43, 44, 94, and 96) were monitored with the thermogravimetric parameters. An absolute quantification in this work was performed for each monitored gases: CH_4, CO_2, CO, C_2H_4, NH_3, O_2, C_6H_6O, CH_2O, $C_2H_4O_2$, and CH_5O_3P. The concentrations of CH_4, CO_2, CO, C_2H_4, NH_3, O_2, C_6H_6O, CH_2O, $C_2H_4O_2$, and CH_5O_3P were directly deduced from the partial pressure of gases by using Eq. (77.1).

$$[A_i] = (P_i/P_T) \times 1\,000\,000 \tag{77.1}$$

Where, $[A_i]$ is the concentration of the gas A, Pi is the partial pressure for m/z = i representing of gas A, and P_T is the total pressure for all species i.

Results and Discussion

Proximate Analysis

Table 77.1 shows the proximate analysis of the biomass used in this study. Moisture content, volatile matter and fixed carbon were determined using TGA analysis. However, ash content was investigated as per ASTM Standard Method E1755-01. Low moisture content in the present biomass suggests them as a good candidate for torrefaction process. Switchgrass showed highest amount of volatile matter and lowest fixed carbon content compared to other biomass. Agricultural biomass showed high amount of ash content compared to forestry biomass. The same comparison in the ash content was reported for agricultural biomass and woody biomass [20].

TG-DTG Analysis

Figure 77.1 depicts the thermogravimetric curve for different biomasses. The degradation reactivity for forestry biomass (spruce and pine) was almost similar to each other. However the degradation behavior of switchgrass differed from other biomass. The initial decrease in the weight loss of biomass was attributed to removal of moisture content up to temperature 110 °C. The initial degradation temperature for spruce, pine, and timothy was about 210 °C. Whilst for switchgrass it was about 175 °C. This shows that the decomposition of switchgrass took place earlier compared to other biomass. From the TGA, the final degradation temperature for spruce, pine, switchgrass, and timothy was about 375, 375, 360, and 380 °C, respectively. Between temperatures 200 and 500 °C higher decomposition of cellulose and hemicellulose might have occurred, while small amount of lignin degradation is expected to take place. This observation was reported similarly for various woody biomasses [7]. No significant weight loss was observed after temperature of 500 °C. The residual or biochar content for spruce, pine, switchgrass, and timothy was about 16, 15, 21, and 11 wt%, respectively.

Apparently, switchgrass showed a highest total weight loss at temperature 800 °C. With respect to the torrefaction temperature of about 300 °C, switchgrass showed highest weight loss of about 30 wt% compared to spruce (17 wt%), pine (20 wt%), and timothy (20 wt%). This shows that switchgrass can be an attractive raw material for torrefaction. According to previous studies [3] and [11], the thermal decomposition of hemicellulose, cellulose and lignin occurs at temperatures ranging from 150 to 350, 275 to 350, and 250 to 500, respectively. Similarly, the decomposition of lignocellulosic materials in four biomasses is presented in Fig. 77.2.

Figure 77.2 shows that agricultural biomass has two peaks as contrast to one peak for the forestry biomass. The first peak is attributed due to degradation of hemicellulose. However, second peak represent the decomposition of cellulose. The first and the second peak for switchgrass were found at temperature of about 230 and 330 °C, respectively. In the case of timothy it was found at temperature of about 310 and 355 °C, respectively. The DTG peaks for forestry biomass (spruce and pine)

Table 77.1 Proximate analysis data of selected biomass materials (% weight dry)

	Spruce	Pine	Switchgrass	Timothy
Moisture (%)	2.92	4.63	2.23	2.82
Volatile matter (%)	73.75	73.05	68.46	79.55
Fixed carbon (%)	23.33	22.32	25.70	13.57
Ash (%)	Trace	Trace	3.61	4.06

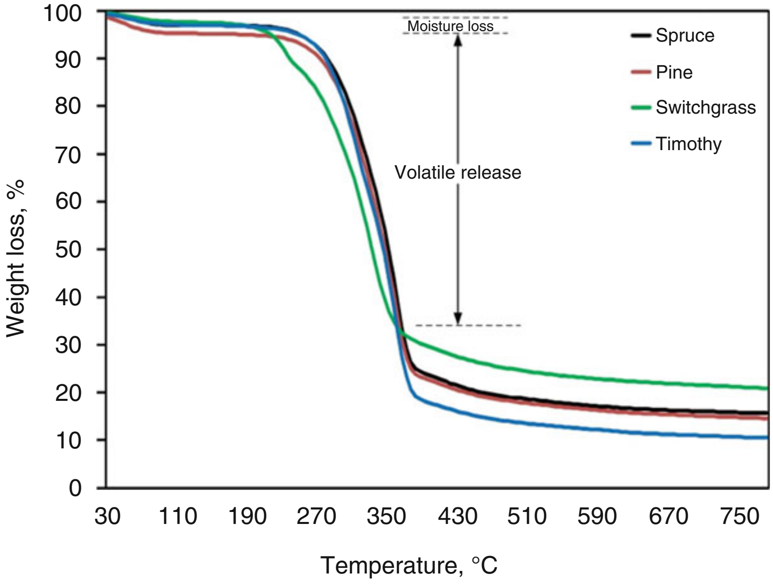


Fig. 77.1 Thermo-diagram of biomass in nitrogen atmosphere, the loss of moisture, volatiles and char

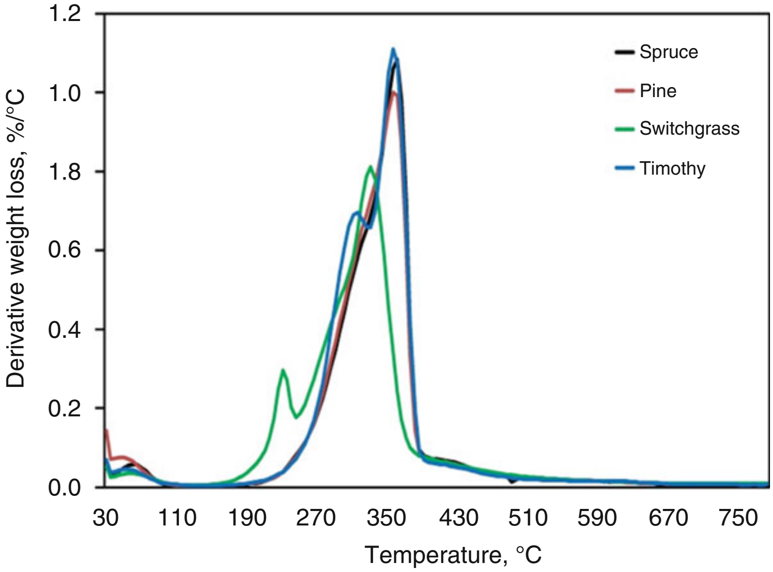


Fig. 77.2 DTG curves of biomass

was at temperature 350 °C. From this observation, it can be concluded that the hemicellulose content in the softwood biomass is less compared to agricultural biomass. A kinetic study on willow and agricultural biomass was found that willow has less hemicellulose content compared to reed canary grass and wheat straw [5].

FTIR Analysis

Figures 77.3, 77.4, 77.5, and 77.6 illustrates the possible chemical functional groups of the torrefied biomass. The FTIR spectra shown in Figs. 77.3, 77.4, 77.5, and 77.6 correspond to the gas analyzed at different torrefaction temperature of 200, 230, 260, and 290 °C, respectively. Overall, the peaks for different functional groups became more sharp and visible when the temperature was increased from 200 to 290 °C. This shows that at higher temperature around 300 °C more degradation of biomass took place. The band around 3,600–3,400 cm^{-1} is apparently due to hydroxyl (O–H) groups, which was found in all torrefied biomass. The C–H stretch band around 2,970–2,780 cm^{-1} is the indication of an organic compound. A sharp band around 2,300–2,200 cm^{-1}wave number is due to the formation of CO_2 during torrefaction of biomass. It is observed that the

Fig. 77.3 Decomposition of functional groups at torrefaction temperature 200 °C

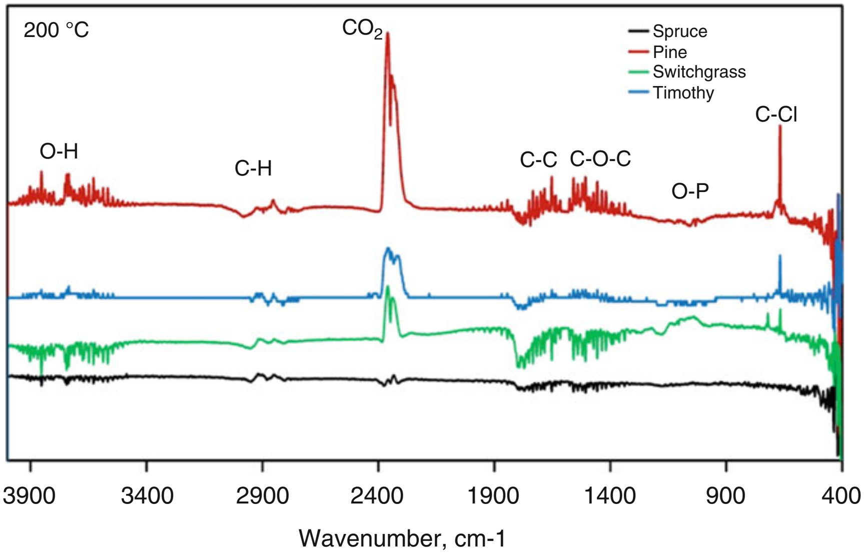
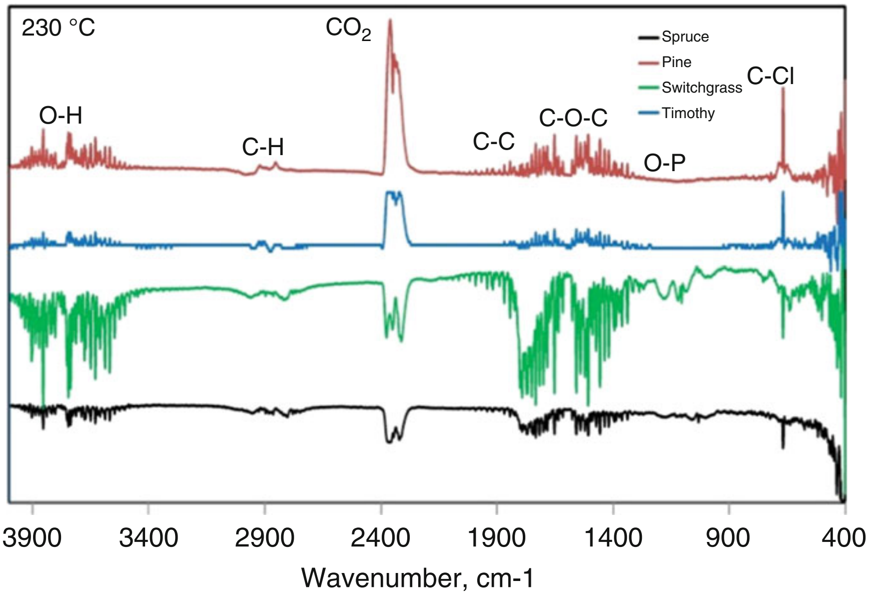


Fig. 77.4 Decomposition of functional groups at torrefaction temperature 230 °C



two major bands in the region of 1,740–1,710 $\text{cm}^{-1}$and 1,250–1,220 cm^{-1} might be because of C–O and C–O–C functional groups, respectively. Organic phosphates (P–O) functional groups can be found in range of 1,350–1,250 cm^{-1} stretch band, and the presented of aliphatic phosphates (P–O–C) functional groups is more obvious at around 1,050–990 cm^{-1} than organic phosphates (P–O) functional groups. A very sharp peak around 730–550 cm^{-1} might be due to acid chlorides (C–Cl) functional groups present [10].

Torrefaction 200 °C

Same procedure was employed for all torrefaction condition; the change of transmittance intensities indicates a variation in the gas concentration [4]. Figure 77.3 shows that pine and switchgrass are more reactive than timothy and spruce at torrefaction temperature 200 ºC, particularly for O–H, C–C, and C–O–C of functional groups. C–H and O=C=O functional groups in all biomass, which are obviously methane (CH_4), and carbon dioxide (CO_2) and carbon monoxide (CO), significantly transmit as they are reactive between 150 and 300 °C [22]. However, different biomass gives out CO_2 and CO at different concentration as shown in Figs. 77.3, 77.4, 77.5, and 77.6. CO_2 from spruce is the lowest in concentration compared to pine, switchgrass, and timothy at torrefaction temperature 200 ºC. Switchgrass shows significant C–O–P and

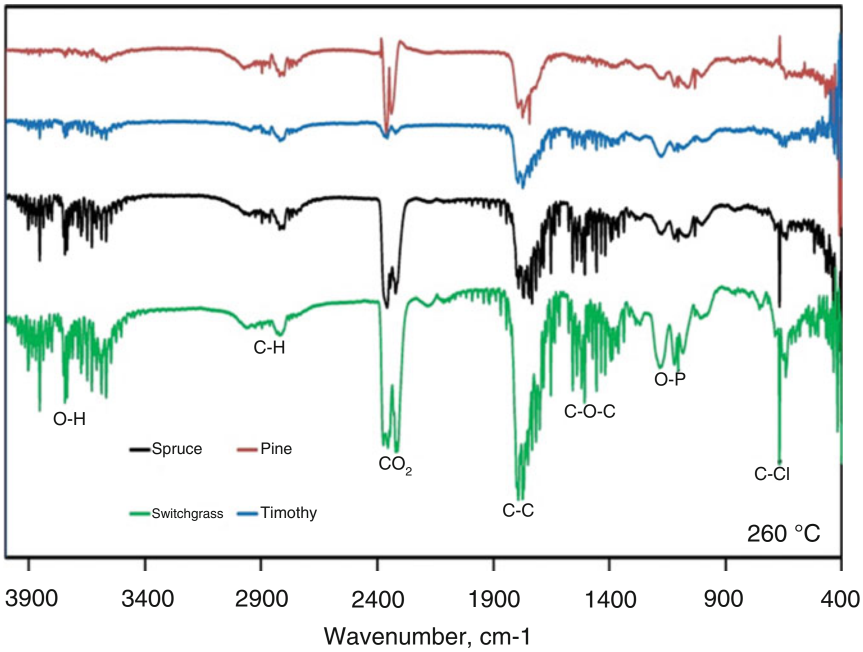


Fig. 77.5 Decomposition of functional groups at torrefaction temperature 260 °C

O–P groups than the others. Organochlorine compounds (C–Cl functional groups) are normally present in plants and wood. Its reactivity varies enormously, but most are relatively inert. However, this functional group has shown different concentration from different biomass. The intensity at torrefaction temperature 200 ºC is at the highest in pine compared to switchgrass and timothy, and seemingly none from spruce.

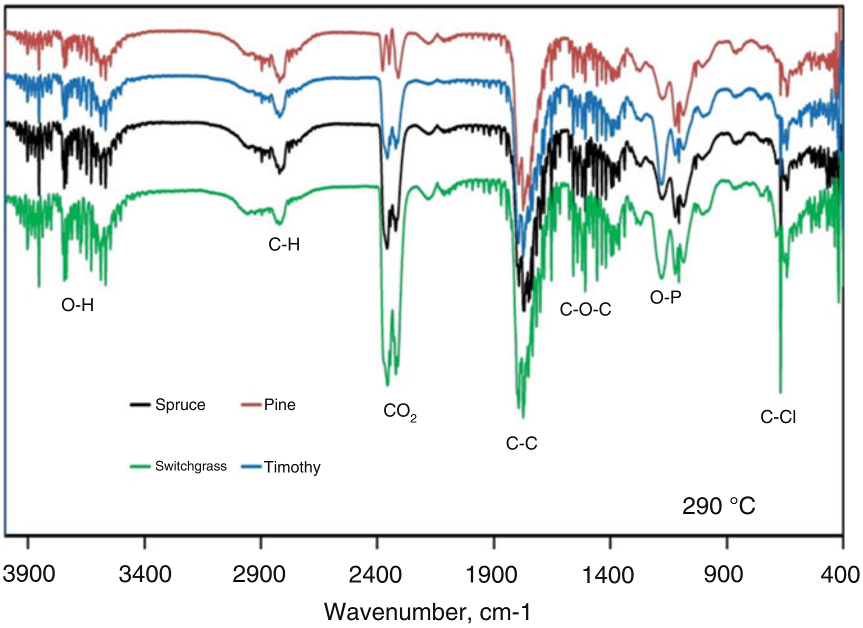
Torrefaction 230 °C

As at torrefaction temperature 200 ºC, most functional groups significantly transmitted at torrefaction 230 ºC but at different level of intensity. Figure 77.4 shows, the chemical compounds in switchgrass are the most reactive compared to the one in pine, spruce, and timothy. O–H, C–C and C–O–C of functional groups in particular, an increase in the intensity were transmitted from torrefaction temperature 230 ºC. The release of CO_2 at torrefaction temperature 230 ºC is about the same as at torrefaction temperature 200 ºC for pine, switchgrass, and timothy. However, the CO_2 release from spruce has increased at this torrefaction temperature. At torrefaction temperature 200 ºC, as well as torrefaction temperature 230 ºC, the phosphate compounds released significantly only from switchgrass, and apparently none from the other biomass. Organochlorine compounds (C–Cl functional groups) are released from all biomass at this torrefaction temperature, but the transmittance still at different intensity. Pine and switchgrass released almost of this compound at torrefaction temperature 230 ºC.

Torrefaction 260 °C

From Fig. 77.5, pine and timothy were found has less reactive as compared to spruce and switchgrass. The transmittance intensity for spruce has shown significant increased at torrefaction temperature 260 ºC from the torrefaction temperature 200 and 230 °C. The intensities of all the functional groups of chemicals for spruce were just a slight lesser than switchgrass. This can be anticipated that the degradation of spruce, pine, and timothy were engaged at later temperature than that of switchgrass. This might be almost hemicellulose and partially cellulose from switchgrass easily released at lower torrefaction temperature (200, 230 and 260 °C) due to less lignin content to bind them from devolatilization and depolymerization [8, 14, 24]. Lignin decompose from temperature 280 ºC and difficult to dehydrate. Thus it converts to more char and loose the covalent bond to cellulose or hemicelluloses [24]. The releases of CO_2 from switchgrass and spruce at torrefaction temperature 260 ºC were higher than that of lower torrefaction temperature (200 and 230 ºC). Switchgrass was also identified giving off the gases (functional groups O=C=O) the highest among the selected biomasses at torrefaction temperature 260 °C. The phosphate compounds were gradually degraded at this torrefaction temperature from torrefaction temperature 200 and 230 °C for all biomass. Organochlorine compounds (C–Cl functional groups) released from spruce and switchgrass significantly greater than that from pine and timothy.

Fig. 77.6 Decomposition of functional groups at torrefaction temperature 290 °C



Torrefaction 290 °C

It is clearly shown from Fig. 77.6, the transmittance intensities of all the selected functional groups were significantly high which means almost gases and organic compound were degraded at torrefaction temperature 290 ºC. The released intensities of O–H, C–H, O=C=O, C–C, C–O–C, and O–P functional groups were found greater at torrefaction temperature 290 °C than that of at lower torrefaction temperature. The lignocellulosic biomass has converted to carbonaceous materials due to generous hemicellulose and cellulose was degraded at this torrefaction temperature. The organochlorine compounds (C–Cl functional groups) and gases (O=C=O functional groups) released from switchgrass were still significantly greater than that of spruce, pine, and timothy.

Gas Quantification

FTIR and mass spectrometric analyses have advantages and disadvantages. Using information provided by the FTIR spectrum is possible to have an identification of the gases emitted by each biomass. However, quantification of each emitted gases require specific tool or software to measure. TG-FTIR and TG-MS techniques are therefore complementary since they can refine the identification of gases. Table 77.2 shows the concentration of each gas during torrefaction of the selected biomass as the results from the TG-MS. To compare the evolution of gas emissions during torrefaction, the gas composition was calculated as a function of temperature. The comparison is made upon the gas concentration released by the biomass, which the yields of the gases were calculated for the four range of torrefaction temperature (Table 77.2). From the table all the four stages of temperature, the degradation of gases are mainly composed on O_2, CO_2, and CO, and then are followed by C_2H_4, NH_3, CH_2O and CH_4. Carbolic acid, acetic acid and phosphonic acid have the lowest degradation during the torrefaction. Switchgrass has degraded carbon dioxide and carbon monoxide the highest compared to spruce, pine, and timothy. These results are in agreement with the FTIR spectrum, which the functional group showed among the highest of transmittance for switchgrass. The C-H functional group in the FTIR spectrum has depicted about the same transmittance intensities for all the biomass. The mass spectrum analysis found for these same intensities was attributed due to the methane (CH_4) generated from switchgrass, timothy, and pine, and ethylene (C_2H_4) generated from spruce. Simple gas molecule O_2 does not have infrared spectra, which cannot be scanned by FTIR. MS has this advantage on O_2 that has shown in this study the amount composed in biomass is as high as other main composition such as H_2O (depicted in FTIR spectrum). The main composition of volatile products released from biomass was identified as H_2O, CO, CO_2 [22], which was found to be the same in this study including O_2. Pine has generated the oxygen at the highest concentration as compared to switchgrass, timothy, and spruce. Generally, the concentration of the selected gas degradation emitted during torrefaction is around 20–35 % of the total concentration for all biomass, but vary in the propositions when compare between biomass and stages of

Table 77.2 Concentration of selected gaseous products evolved from torrefaction of spruce, pine, switchgrass, and timothy

		Methane (mg CH_4/g biomass)				*Carbon dioxide (mg CO_2/g biomass)*			
	Temp. (°C)	*Spruce*	*Pine*	*SW*	*Timothy*	*Spruce*	*Pine*	*SW*	*Timothy*
Residence time 30 min	200	0.015	0.02	0.023	0.024	0.017	0.036	0.02	0.043
	230	0.018	0.023	0.027	0.028	0.019	0.042	0.028	0.05
	260	0.021	0.026	0.032	0.032	0.025	0.05	0.039	0.058
	290	0.024	0.03	0.036	0.036	0.031	0.063	0.061	0.068
Total[a] of 81 min	30–800	0.07	0.088	0.110	0.105	0.171	0.284	0.339	0.341
		Carbon monoxide ($\times 10^{-2}$ g CO/g biomass)				*Ethylene (mg C_2H_4/g biomass)*			
	Temp. (°C)	*Spruce*	*Pine*	*SW*	*Timothy*	*Spruce*	*Pine*	*SW*	*Timothy*
Residence time 30 min	200	0.074	0.11	0.143	0.121	0.041	0.02	0.017	0.02
	230	0.087	0.128	0.166	0.141	0.047	0.022	0.02	0.024
	260	0.098	0.146	0.189	0.16	0.054	0.025	0.023	0.028
	290	0.111	0.164	0.214	0.18	0.06	0.028	0.026	0.031
Total[a] of 81 min	30–800	0.309	0.454	0.575	0.511	0.167	0.074	0.081	0.092
		Ammonia (mg NH_3/g biomass)				*Oxygen (mg O_2/g biomass)*			
	Temp. (°C)	*Spruce*	*Pine*	*SW*	*Timothy*	*Spruce*	*Pine*	*SW*	*Timothy*
Residence time 30 min	200	0.035	0.041	0.04	0.042	0.181	0.324	0.258	0.231
	230	0.04	0.046	0.046	0.049	0.209	0.36	0.299	0.269
	260	0.046	0.051	0.053	0.055	0.236	0.393	0.34	0.305
	290	0.052	0.057	0.06	0.063	0.262	0.428	0.381	0.342
Total[a] of 81 min	30–800	0.152	0.16	0.18	0.183	0.589	0.916	0.896	0.854
		Phenol (mg C_6H_6O/g biomass)				*Formaldehyde (mg CH_2O/g biomass)*			
	Temp. (°C)	*Spruce*	*Pine*	*SW*	*Timothy*	*Spruce*	*Pine*	*SW*	*Timothy*
Residence time 30 min	200	0.006	0.007	0.007	0.009	0.034	0.026	0.027	0.027
	230	0.007	0.008	0.008	0.011	0.044	0.03	0.032	0.032
	260	0.008	0.009	0.009	0.013	0.046	0.034	0.037	0.036
	290	0.009	0.01	0.01	0.014	0.047	0.039	0.043	0.042
Total[a] of 81 min	30–800	0.023	0.028	0.029	0.035	0.155	0.125	0.135	0.135
		Acetic acid (mg $C_2H_4O_2$/g biomass)				*Phosphonic acid (mg CH_5O_3P/g biomass)*			
	Temp. (°C)	*Spruce*	*Pine*	*SW*	*Timothy*	*Spruce*	*Pine*	*SW*	*Timothy*
Residence time 30 min	200	0.006	0.008	0.009	0.009	0.005	0.007	0.007	0.009
	230	0.007	0.01	0.01	0.011	0.006	0.008	0.008	0.01
	260	0.008	0.011	0.012	0.013	0.007	0.009	0.009	0.012
	290	0.009	0.013	0.014	0.014	0.008	0.01	0.011	0.013
Total[a] of 81 min	30–800	0.037	0.045	0.05	0.049	0.024	0.028	0.031	0.035

[a] *Note*: The continuous torrefaction from room temperature to 800 °C

torrefaction temperatures. For the continuous torrefaction range of temperature, the degradation of combustible gases (CH_4, CO, C_2H_2, O_2) released by switchgrass (1.662 mg/$g_{switchgrass}$) is more than timothy (1.562 mg/$g_{timothy}$), pine (1.532 mg/g_{pine}), and spruce (1.135 mg/g_{spruce}). The degradation of combustible gases during torrefaction temperature 200, 230, and 260 °C by pine showed the highest (0.474, 0.533, and 0.590 mg/g_{pine}, respectively) as compared to switchgrass (0.441, 0.512, and 0.584 mg/$g_{switchgrass}$, respectively), timothy (0.396, 0.462, and 0.525 mg/$g_{timothy}$, respectively), and spruce (0.311, 0.361, and 0.409 mg/g_{spruce}, respectively). Whilst, for torrefaction temperature 290 °C, the degradation of combustible gases has similar trend as for continuous torrefaction range of temperature that is switchgrass took place the highest (0.657 mg/$g_{switchgrass}$) as compared to pine (0.650 mg/g_{pine}), timothy (0.587 mg/$g_{timothy}$), and spruce (0.457 mg/g_{spruce}). For all species, the percentages of combustible gases may increases significantly after 300 °C, and thus, loose the energetic content of the biomass.

Conclusion

Four different types of Canadian biomasses were torrefied using TGA-FTIR analyzer and TGA-Mass spectrometry. Forestry and agriculture biomass showed single and two DTG peaks respectively during torrefaction. It was observed that the species had different evolution patterns, which indicates the presence of different chemical functional groups within the biomass samples. In general, TG-FTIR analysis showed that the torrefaction behavior of forestry (spruce and pine) biomass were similar. Of all the biomass, switchgrass experienced considerable weight loss at lower torrefaction temperature. Pine, timothy, and spruce were found to have similar degradation behavior in terms of chemical functional groups when torrefied at lower temperature (200 and 230 °C). Degradation of combustible gases: CH_4, CO, C_2H_2, and O_2, during torrefaction at lower temperature: 200 and 230 °C is around 20–30 %, whilst at temperature 260 and 290 °C is around 30–45 %. Most of the chemical compositions were decomposed at higher torrefaction temperature of 290 °C. Overall, the gaseous products evolved during torrefaction of forestry and agricultural biomass showed similar FTIR spectra patterns and in agreement with mass spectrometric, MS, with regard to the degradation of combustible gases. Torrefaction temperature played a key role in the formation of these gaseous products.

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